

Water–Alcohol Separation by Pervaporation Through Poly(amide-sulfonamide)s (PASAs) Membranes

WING-HONG CHAN, CHING-FAI NG, SUEI-YEE LAM-LEUNG, XUMIN HE, ON-CHEUNG CHEUNG

Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Kowloon, Hong Kong

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ABSTRACT: Pervaporation membranes derived from seven homopolymers of poly(amide-sulfonamide)s (PASAs) were prepared by casting 10–17% polymer solutions of *N,N*-dimethylacetamide. The membranes were characterized by sorption experiments, scanning electron microscope, and wide-angle X-ray diffraction. During the pervaporation of 90 wt % aqueous solution of methanol, ethanol, 1-propanol, and 2-propanol, all membranes were preferentially permeable to water, and their separation factors were mainly dependent on the molecular weight of the solvent. The exact structure of the PASAs had a profound effect on their pervaporation characteristics. Polymeric membrane based on *N,N'*-bis(4-aminophenylsulfonyl)-1,3-diaminopropane and isophthaloyl chloride exhibited the best selectivity factor of 1984 for a 10 : 90 (by weight) mixture of water/ethanol at 20°C. However, the permeation rates of all materials for dehydration of 90 wt % ethanol were slow in a range of 6.6–34.4 g m⁻² h⁻¹. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1113–1119, 1997

Key words: poly(amide-sulfonamide)s; water-permeable membrane; symmetric nonporous membrane; pervaporation; water–alcohol separation

INTRODUCTION

Membrane technology represents one of the most effective and energy-saving means to a wide range of separation processes.¹ Although technological innovation may result in widening the scope of applications of the technology, the needs for searching new polymeric materials for membrane applications have been a continuous research challenge.^{2–6} For instance, with regard to the development of new materials, the U.S. Department of Energy identified “pervaporation membrane for organic–organic separations” and “reverse osmosis oxidation-resistant membrane” as two of the highest ranking research priorities.⁷ In response to this research challenge, we have designed and synthesized a series of new poly(amide-sulfonamide)s (PASAs).^{8–10} In general, this class of new

materials possesses several desirable membrane properties: reasonably high intrinsic viscosity able to fabricate tough membrane; high chemical stability resistant to attack of corrosive chemicals; and enough hydrophilicity to be advantageous to the permeation of water flux. Furthermore, the potential of this membrane material used in the reverse osmosis process has been explored in our laboratory.¹¹ On the other hand, over the past 10 years, membrane pervaporation has emerged for the chemical industry as an effective process tool for separation and recovery of liquid mixture, including dehydration of alcohols. In this study, symmetric nonporous membranes of different PASAs were prepared and adequately characterized. Their pervaporation separation characteristics toward a variety of aqueous alcohol mixtures were established. The relation between the structure of the polymers and their permselectivity in the pervaporation process is discussed. The effects of degree of swelling, degree of crystallinity in polymers, and operation temperature on the perva-

Correspondence to: Wing-hong Chan.

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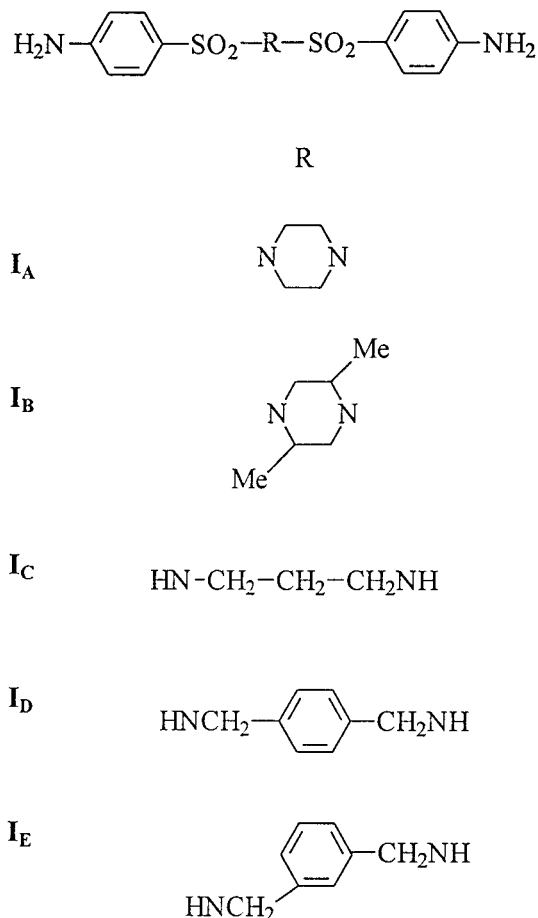


Figure 1 Structure of diamino monomer **I_A–I_E**.

poration performances of selected PASA membranes are studied.

EXPERIMENTAL

Materials

PASAs of a variety of structures were obtained by low-temperature solution polycondensation of the respective diamines (**I_A–I_E**) (Fig. 1) with terephthaloyl chloride/isophthaloyl chloride, as reported elsewhere.⁹ *N,N*-Dimethylacetamide (DMAc) (Fluka) was dried over 4 Å molecular sieves.

Membrane Preparation

Depending on the intrinsic viscosity of each of the polymers, the respective casting solutions of PASAs were prepared by dissolving the polymers in dried DMAc at different compositions (Table

I). The casting solutions were allowed to stand at room temperature until complete dissolution of the polymers. To remove suspended impurities, the solutions were suction filtered through a sinter glass funnel (Pyrex G2). Membranes were obtained by pouring the PASA casting solutions onto a glass plate, then spreading by a glass rod with two ends coiled with rings of 0.315-mm diameter copper wire. The membrane on the glass plate was heated on a preheated hot plate at 70°C for 30 min to slowly evaporate the solvent, then cooled to room temperature in a period of 30 min. Nonporous membranes with a thickness of ~20 μm were obtained by putting the glass plate into a deionized water bath. The membranes could be stored dry when not in use. Prior to use, membranes were immersed in a solvent mixture whose composition was comparable to the feed solution.

MEASUREMENTS

Sorption

The degree of swelling (DS; %) of the membrane was defined by the following equation:

$$\text{DS} = \left(\frac{\text{Weight of swollen membrane}}{\text{Weight of dry membrane}} - 1 \right) \times 100\%$$

The weight of a dry membrane was obtained by first taking the constant weight of the membrane which had been dried in vacuum oven at 60°C over 24 h. Then the dried membrane was immersed in deionized water, water–ethanol mixture, or absolute ethanol, respectively, at 20°C for 1 week. After achieving the swelling equilibrium, the free liquid was removed from the surface of the swollen membrane using filter paper, and the membrane was again weighed to obtain the weight of the swollen membrane.

Crystallinities

Wide-angle X-ray diffraction (WAXD) data of polymer thin films prepared from dilute DMAc solutions of the polymers were obtained at room temperature on a Rigaku D-MAX apparatus using nickel-filtered CuK_α radiation (40 kV, 40 mA).

Pervaporation Experiment

The pervaporation apparatus fabricated in-house is shown in Figure 2. Its upper compartment, with

Table I Formulation of Various PASA Casting Solutions

Polymer	Diamino Monomer	Diacid Chloride ^a	$[\eta]_{\text{intrinsic}}$ (dL g ⁻¹) ^b	Concentration of Casting Solutions (wt %)
II _{AM}	I _A	B	0.85	12.0
II _{BM}	I _B	B	0.85	12.0
II _{CP}	I _C	A	1.20	10.5
II _{CM}	I _C	B	1.36	10.0
II _{DM}	I _D	B	0.85	12.0
II _{EP}	I _E	A	1.21	10.5
II _{EM}	I _E	B	0.75	17.0

^a A, terephthaloyl chloride; B, isophthaloyl chloride.

^b Viscosity in DMAC solution at 25.00 ± 0.05°C.

a capacity of 300 cm³, containing the liquid feed mixture, was equipped with a magnetic stirrer, a thermometer, and a heating spiral connected to a circulating thermostatted bath. The membrane used, which was 6.5 cm in diameter, was fixed in a stainless steel pressure holder. A constant downstream pressure was maintained at 0.5 torr Hg by a vacuum pump (Edwards). The permeate sample was condensed and collected in a cold-trap cooled with liquid nitrogen for 7 h. Most of the pervaporation experiments were carried out at 20°C, while some were performed in the temperature range of 20–60°C to observe the temperature dependence of the process.

To fix the feed composition constant, the mass of permeate collected during a run was kept small compared with the mass of the feed. The separation analysis was carried out on a Shimadzu GC-8A gas chromatography equipped with a 1-m long column packed with Hayesep DB.

Two parameters were used to evaluate the performance of a pervaporation run:

1. The permeation flux, J , was obtained by

$$J = \frac{Q}{A \cdot t} \quad (1)$$

where Q is the total amount (g) permeated sample collected during an experiment time interval t (h), and A (m²) is the effective surface area of the membrane.

2. The selectivity factor α , illustrated by a dehydration of ethanol process, defined as

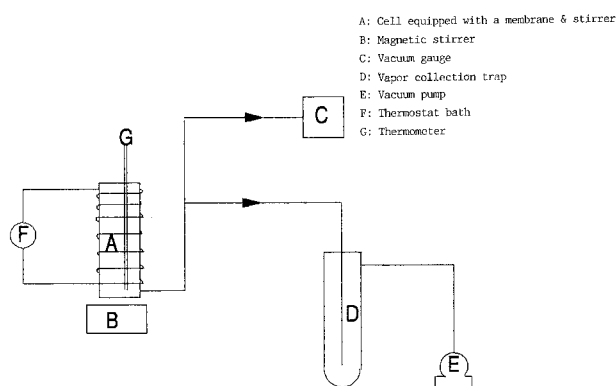
$$\alpha = \frac{Y_{\text{water}}/Y_{\text{ethanol}}}{X_{\text{water}}/X_{\text{ethanol}}} \quad (2)$$

where X and Y denote the weight fraction of water and ethanol in the feed solution and in the pervaporate, respectively.

RESULTS AND DISCUSSION

PASA Pervaporation Membranes

In our initial investigation, 14 new homopolymers of PASAs were synthesized via a three-step reaction sequence.⁹ Seven of them were found to be tough enough to be amenable to membrane applications, and thus were selected for this study (Table I). Both the sulfonamide and amide groups present in the backbone of the polymer chains enable the polymer to have favorable interactions with water molecules through hydrogen bonding in a separation process. The reasonable water flux rate observed for PASA membranes in the RO process reported elsewhere supported this claim.¹¹ Thus, at the outset of this work, we believed that PASAs would be a viable material to prepare hydrophilic dehydration membranes applicable to pervaporation processes.²

**Figure 2** Pervaporation apparatus.

Because the intrinsic viscosity of the synthesized polymeric materials in our hand was quite varied, the concentration of each polymer in the casting solutions was needed to be adjusted in a range of 10.0–17.0%. The higher the intrinsic viscosity of the polymer, the lower its concentration required in the casting solution. On the other hand, as a consequence of the membrane fabrication conditions adopted in this study, we expected a symmetric nonporous membrane would result. A limiting membrane thickness value of $\sim 15\ \mu\text{m}$ was deemed to be appropriate for pervaporation membranes to exhibit stable performance.¹² Therefore, we intended to control the thickness of membranes well above the limiting value. Figure 3 shows the scanning micrograph of a representative PASA membrane. The cross section of the membrane [Fig. 3(a)] indicated that the membrane thickness in fact was controlled at $\sim 20\ \mu\text{m}$, which agreed well with the micrometer measurement. Furthermore, the scanning electron microscope study manifested the nonporous and symmetric nature of the membrane. In fact, the morphology of the membrane at both faces was very similar [Fig. 3(b,c)]. Most of the PASA membranes were semitransparent and could be stored under dry conditions for an extended period of time prior to their use.

Sorption

The DS of the membranes in 90% and 50% of ethanol–water solutions was quite substantial, and in most of the cases exceeded 10% (Table II). The extent of swelling of all PASA membranes was found to be greater in pure ethanol than in pure water. Nevertheless, some of them (i.e., II_{AM} and II_{BM}) were quite “hydrophilic” with the DS in water well above 8%. The manifested water affinity of PASAs could be attributable to the ability of sulfonamide and acid amide moieties in the polymer backbone to form hydrogen bonds with water molecules.

Crystallinities

In a glassy polymer like PASA, the permeability of the components was controlled by their diffusivity in the polymer system.¹³ Furthermore, the presence of crystallites in the polymer matrix would deter the permeability of the penetrating molecules,¹⁴ which in turn may slow down the permeation flux of the pervaporate. Therefore, it is of great significance to assess the degree of crys-

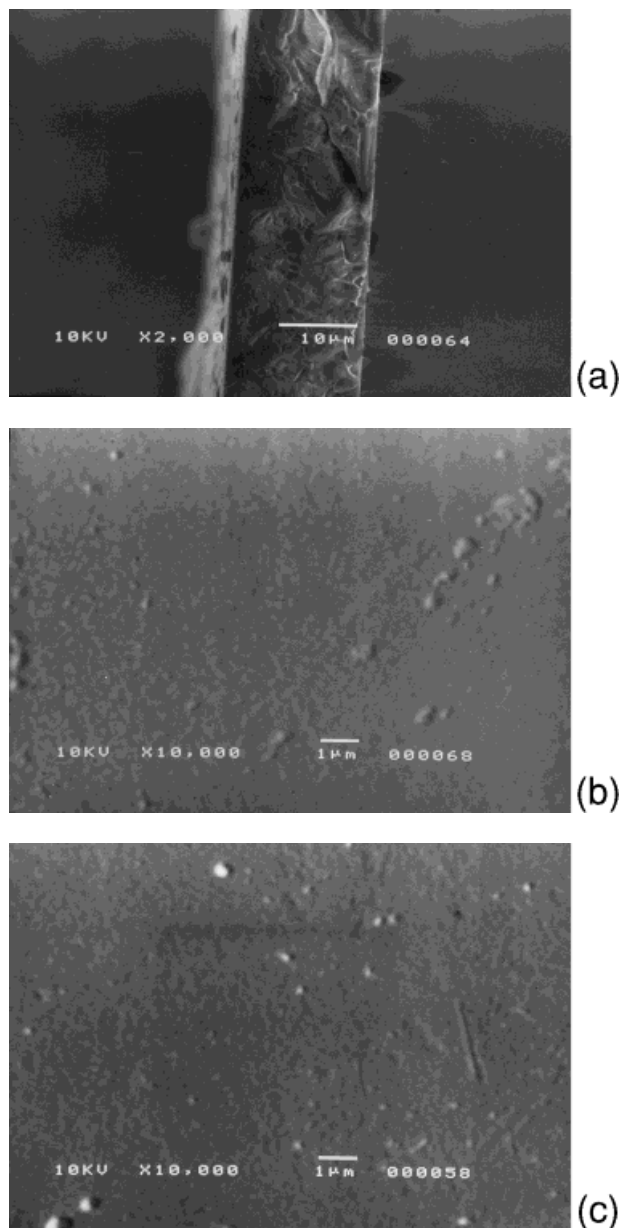


Figure 3 Scanning electron microscope pictures of (a) the cross section; (b) the top surface; and (c) the bottom surface of a II_{BM} membrane.

tallinity in the polymer system. The degree of crystallinity for the PASA membranes was investigated by X-ray ($2\theta = 5\text{--}40^\circ$). The results obtained for different polymer membranes are shown in Figure 4. Apparently most of the PASAs demonstrated a certain degree of crystallinity. Completely amorphous polymer was not found in these PASAs. Most of the polymers in this study exhibited two strong peaks at $\sim 9^\circ$ and 19° . The relatively low permeation flux rate observed for

Table II Degree of Swelling (%) of PASAs in Water, Ethanol, and Aqueous Ethanol Solution

Polymer	Water	Water/Ethanol (1 : 9)	Water/Ethanol (5 : 5)	Ethanol
II _{AM}	9.99	13.31	16.81	15.98
II _{BM}	8.52	13.00	14.94	17.37
II _{CP}	6.99	12.08	13.54	15.84
II _{CM}	6.33	11.78	12.87	16.12
II _{DM}	5.70	9.55	10.84	14.19
II _{EP}	6.97	9.96	9.40	11.94
II _{EM}	4.16	7.38	9.61	7.97

PASA membranes was consistent with the presence of crystallites in the polymer matrix.

Pervaporation Properties

The pervaporation process combines the evaporation of volatile components of a mixture with their permeation through a polymeric membrane by a solution-diffusion mechanism under reduced pressure conditions. Separation characteristics of a membrane depend on three major factors with regard to the constituents of the mixture: affinity to the membrane, bulkiness of the molecule, and vapor pressure. The affinity of volatile components to the membrane can be evaluated by the sorption experiments (*vide supra*). During the pervaporation of 90% aqueous solutions of low-

molecular-weight alcohols, membranes derived from PASAs were preferentially permeable to water (Table III), even though the sorption experiments showed that the swelling ratio of ethanol onto membranes was greater than that of water. These results indicated the process was diffusion control, which was in good agreement with the pervaporation properties of other glassy polymeric materials.¹³ Huang and Jarvis¹⁵ demonstrated that, as the molecular weight of permeated molecules in a given homologous series increases, the permeation flux decreases and the separation increases. The present work shows that the same relationship holds for the homologous series of methanol, ethanol, 1-propanol, and 2-propanol using PASA membranes. Table III shows that the permeation flux of each of the PASA membranes though small increases as the bulkiness of the penetrating molecules decreases. Membrane selectivity is also found to depend on the size of the alcohol molecules. Exceptionally excellent separations of the water-propanol mixture were observed for all materials.

The structure variation in the PASAs series had a profound effect on their pervaporation properties. For instance, the viscosity of **II**_{AM} and **II**_{BM} are very close, yet the former material clearly possesses a better selectivity toward water-alcohol mixture than the latter. This difference can be attributed to the fact that in a diffusion-control process without the appendage of two methyl groups to the piperazine ring, the more compact nature of **II**_{AM} would enhance its separation power over that of **II**_{BM}. On the other hand, polymer **II**_{CP} contains the most compact backbone, allowing close packing of polymer chains, which exhibits the best discriminating power toward water-alcohol mixtures, albeit an extremely low flux rate. Among all PASAs, **II**_{BM} emerged as the best pervaporation material which exhibits a good combi-

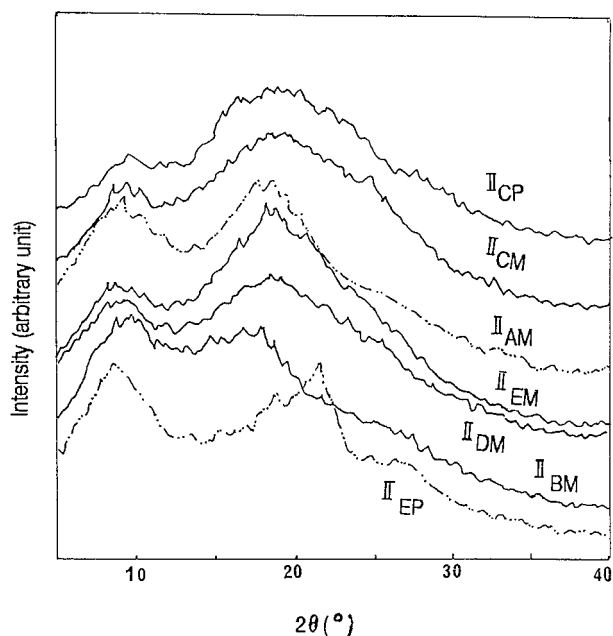


Figure 4 X-ray diffraction diagrams obtained from different PASA membranes.

Table III Pervaporation of Aqueous Solutions of Low Molecular Weight Alcohols Through PASA Membranes

Polymer	Water-methanol		Water-ethanol		Water-1-propanol		Water-2-propanol	
	Permeation Flux J ($\text{g m}^{-2} \text{h}^{-1}$)	Selectivity Factor (α_s^w)	Permeation Flux J ($\text{g m}^{-2} \text{h}^{-1}$)	Selectivity Factor (α_s^w)	Permeation Flux J ($\text{g m}^{-2} \text{h}^{-1}$)	Selectivity Factor (α_s^w)	Permeation Flux J ($\text{g m}^{-2} \text{h}^{-1}$)	Selectivity Factor (α_s^w)
Π_{AM}	88.7	4.8	31.3	57.2	19.8	409	21.5	∞
Π_{BM}	67.9	4.1	34.4	39.7	16.4	315	9.5	15116
Π_{CP}	13.3	45.9	8.0	1984	5.6	63084	4.2	∞
Π_{CM}	11.2	26.2	8.3	364	6.8	2507	—	—
Π_{DM}	8.9	26.5	8.0	201	6.6	828	5.3	∞
Π_{EP}	57.8	6.2	12.1	30.2	7.3	550	6.0	2693
Π_{EM}	11.8	46.0	6.6	545	6.0	4303	4.6	∞

Weight percent of alcohol in feed is 90%; pervaporation experiments were carried out at 20°C.

nation of permeability and selectivity in dehydration of alcohols.

Effect of Evaluation Temperature

In order to study the temperature effect on the pervaporation process, Π_{BM} was chosen for de-

tailed work. The effect of evaluation temperature on the separation properties for 87.7 wt % EtOH aqueous solution is shown in Figure 5. With increase of temperature, from 20° to 60°C, the permeation flux had an almost threefold increase while the separation factor changed from 15.78 to 7.34, representing a twofold reduction. As shown

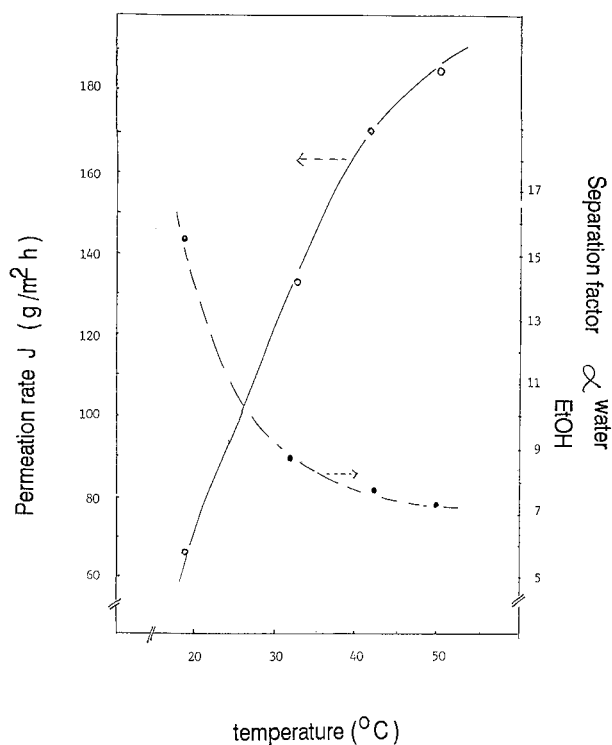


Figure 5 Effect of evaluation temperature on separation properties (Π_{BM} : $\nu_{\text{intrinsic}} = 0.528$; evaluation/pervaporation with 87.7 wt % EtOH).

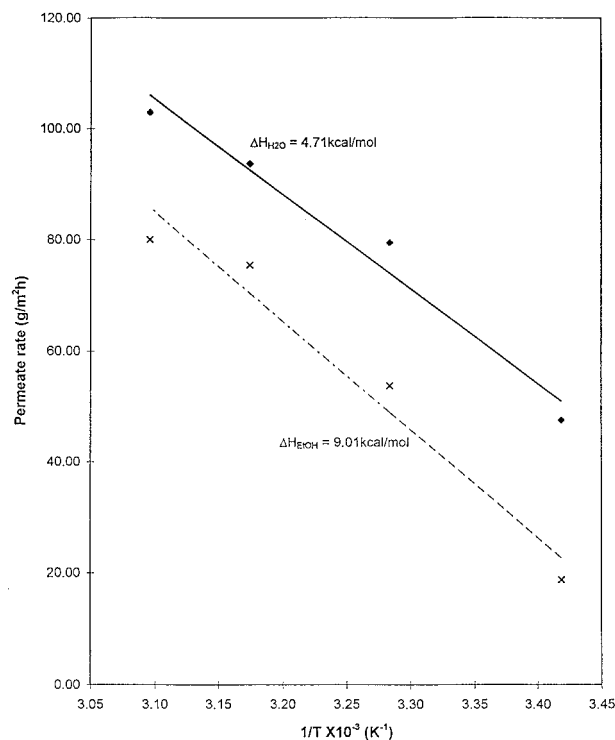


Figure 6 Effect of evaluation temperature on permeation flux (Π_{BM} : $\nu_{\text{intrinsic}} = 0.528$; evaluation/pervaporation with 87.7 wt % EtOH).

in Figure 6, the apparent activation energy ΔE_{app} is 4.71 kcal/mol for water and 9.01 kcal/mol for ethanol. Presumably, the water molecules diffused through the polymer matrix much easier than the ethanol molecules.

CONCLUSIONS

During the evaporation of aqueous solutions of low-molecular-weight alcohols, a variety of PASA symmetric nonporous membranes were found to be preferentially permeable to water. The pervaporation performance of the polymers was related to the structures of the polymers. All the materials exhibited a good-to-excellent selectivity factor for pervaporation separation of water-ethanol.

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